

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 December 2001 (20.12.2001)

PCT

(10) International Publication Number
WO 01/96847 A1

(51) International Patent Classification⁷: **G01N 27/26**,
H01L 29/41, 29/43, D01F 9/12, C01B 31/30

GAO, Bo [CN/US]; 613A Hibbard Drive, Chapel Hill,
NC 27514 (US). SINHA, Saion [IN/US]; 3311 Shannon
Road, #17-B, Durham, NC 27707 (US).

(21) International Application Number: PCT/US01/18846

(74) Agents: GRUDZIECKI, Ronald, L. et al.; Burns, Doane,
Swecker & Mathis, L.L.P., P.O. Box 1404, Alexandria, VA
22313-1404 (US).

(22) International Filing Date: 11 June 2001 (11.06.2001)

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK,
SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA,
ZW.

(25) Filing Language: English

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(26) Publication Language: English

(30) Priority Data:
09/594,844 15 June 2000 (15.06.2000) US

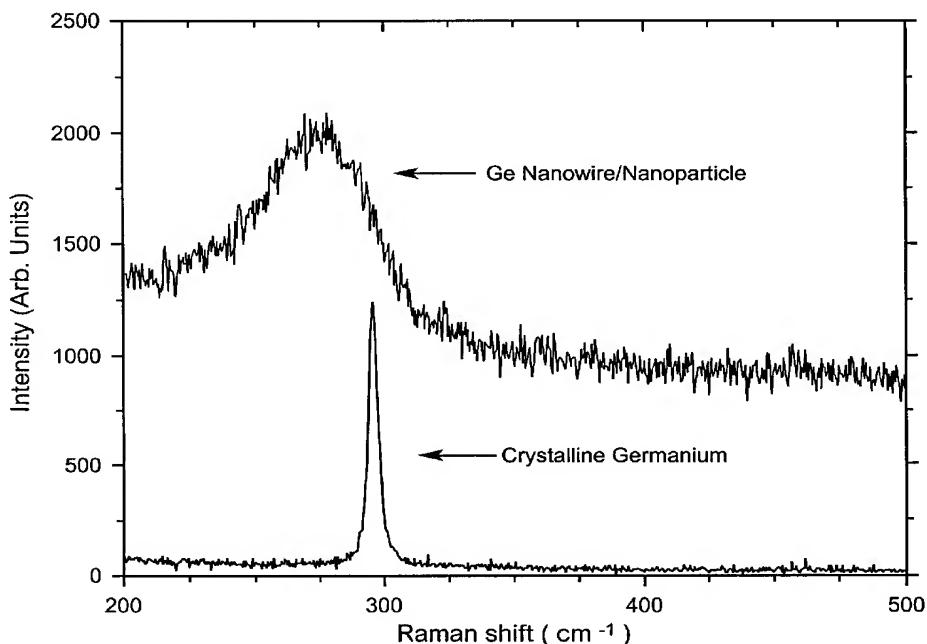
(71) Applicant (*for all designated States except US*): **THE
UNIVERSITY OF NORTH CAROLINA - CHAPEL
HILL** [US/US]; 308 Bynum Hall, Chapel Hill, NC 27599
(US).

[Continued on next page]

(52) Inventors; and

(75) Inventors/Applicants (*for US only*): **ZHOU, Otto, Z.**
[CN/US]; 204 Glenhill Lane, Chapel Hill, NC 27514 (US).

(54) Title: NANOSTRUCTURE-BASED HIGH ENERGY CAPACITY MATERIAL



WO 01/96847 A1

(57) Abstract: A nanostructure based material is capable of accepting and reacting with an alkali metal such as lithium. The material exhibits a reversible capacity ranging from at least approximately 900mAh/g - 1,500mAh/g. The high capacity of the material makes it attractive for a number of applications, such as a battery electrode material.

**Published:**

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*
- *entirely in electronic form (except for this front page) and available upon request from the International Bureau*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

-1-

Nanostructure-Based High Energy Capacity Material

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

5 At least some aspects of this invention were made with Government support under contract no. N00014-98-1-0597. The Government may have certain rights in this invention.

BACKGROUND OF THE INVENTION

10 In the description that follows references are made to certain compounds, devices and methods. These references should not necessarily be construed as an admission that such compounds, devices and methods qualify as prior art under the applicable statutory provisions.

15 With the increasing importance of batteries for a wide variety of uses, ranging from portable electronics to power supply devices for spacecraft, there is a long-felt need for new materials with higher energy densities.

The energy density of a material can be quantified by measuring the amount of electron-donating atoms that can reversibly react with the material. One way of obtaining such a measurement is by setting up an electrochemical cell. The cell comprises a container 20 housing an electrolyte, one electrode made of the electron-donating material (e.g. - an alkali metal), another electrode made of the material whose capacity is being measured (e.g. - a silicon nanostructure-based material), and an electrical circuit connected to the electrodes. Atoms of the electron-donating material undergo an oxidation reaction to form ions of the donating material, and free electrons. These ions are absorbed by the opposite electrode, and 25 the free electrons travel through the electrical circuit. Since the number of electrons "given away" by each atom of the electron-donating material is known, by measuring the number of electrons transferred through the electrical circuit, the number of ions transferred to the material being investigated can be determined. This quantity is the specific capacity of the material, and can be expressed as milliampere-hours per gram of the material. For example, 30 the maximum specific (reversible) capacity of graphite to accept lithium is reported to be approximately 372mAh/g. Because one lithium ion is transferred to the graphite electrode

-2-

for every electron released, the specific capacity can be expressed in terms of the stoichiometry of the electrode material. For graphite, the saturation phase can be characterized as LiC_6 with Li ions residing between the graphene layers. See, for example, (M. Winter et al., Insertion Electrode Materials for Rechargeable Lithium Batteries,

5 Advanced Materials, Vol. 10, 10, "725-762", 1998; and J.R. Dahn et al., Mechanisms for Lithium Insertion in Carbonaceous Materials, *Science*, volume 270, October 27, 1995.

Lithium intercalated graphite and other carbonaceous materials are commercially used as electrodes for advanced Li-ion batteries. See, for example, M.S. Whittingham, editor, Recent Advances in rechargeable Li Batteries, *Solid State Ionics*, volumes 3 and 4, 10 number 69, 1994; G. Pistoria, Lithium Batteries: New Materials, Development and Perspectives, *Elsevier*, 1994. The energy capacities of these conventional battery materials are partially limited by the LiC_6 Li saturation concentration in graphite (equivalent to 372mAh/g).

In order to increase the capacities of electrode materials other carbon based-materials have attracted attention as potential electrode materials. Disordered carbon (soft and hard carbon) materials show reversible lithium storage capacities higher than that obtained from graphite (see, for example, J.R. Dahn et al., Mechanisms for Lithium Insertion in Carbonaceous Materials, *Science*, volume 270, October 27, 1995). Single wall carbon nanotube bundles have a large reversible Li storage capacity of 1000mAh/g, but at a large 20 voltage hysteresis.

Lithium alloys have been investigated as possible anode materials for Li-based batteries. Si and Ge are known to form Li-rich alloys with compositions up to $\text{Li}_{22}\text{Si}_5$ or $\text{Li}_{22}\text{Ge}_5$. They have been investigated for application in high temperature molten salt batteries (see, for example, R.N. Seefurth and R.A. Sharma, Investigation of lithium utilization from a lithium-silicon electrode, *J. Electrochem. Soc.*, Vol. 124, No. 8, 1207-25 1214, 1977). However, electrochemical reaction of Li with Si or Ge is only possible at high temperatures (higher than 350°C).

Pyrolysis of carbon and silicon-containing precursors has yielded materials with enhanced Li storage capacity (500-600mAh/g) (see, e.g.-Carbonaceous materials containing silicon as anodes for lithium-ion cells, *Mat. Res. Soc. Proc.*, Vol. 393, page 305-313, 1995).

-3-

It would be desirable to develop other materials having improved energy storage capacities and energy transfer properties. There exists a long-felt, but so far unfulfilled need, for a material having such properties. There exists a need for a material having improved properties that make it useful in battery electrodes and other high energy applications.

SUMMARY OF THE INVENTION

These and other objects are attained according to the principles of the present invention.

One aspect of the present invention includes a material comprising a nanostructure that can reversibly react with foreign species. The material having a reversible capacity of at least 900mAh/g.

Another aspect of the present invention includes a material comprising silicon rod or wire-like nanostructures and intercalated lithium, the material having a reversible capacity of at least 900mAh/g.

A further aspect of the present invention includes a germanium-based material comprising a germanium and germanium oxide nanostructure. The material having a reversible capacity of at least 1000mAh/g.

In another aspect of the present invention, an article comprising an electrically conductive substrate, and a film deposited on the substrate which comprises any of the above-described materials. The article may take the form of an electrode for a battery.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

Figure 1 is a transmission electron microscope (TEM) micrograph of silicon nanostructures fabricated by a laser ablation method;

Figure 2 is a powder x-ray diffraction pattern of the silicon nanostructures used to store lithium.

Figure 3 is a Raman spectrum of the silicon nanostructures of the present invention;

Figure 4 is a Raman spectrum of the germanium nanostructures of the present invention;

-4-

Figure 5 is a cross-sectional view of a nanostructure-coated substrate according to the present invention;

Figure 6 is an electrochemical cell incorporating an electrode material of the present invention;

5 Figure 7 is a graph showing the charge-discharge characteristics of a silicon nanostructure material formed according to the principles of the present invention;

Figure 8 shows the powder x-ray diffraction and Raman spectra collected from the electrode containing the silicon nanostructures at different stages of the first discharge cycle; and

10 Figure 9 is a graph showing the charge-discharge characteristics of a germanium nanostructure material formed according to the principles of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

A nanostructure-containing material can be formed by a number of techniques 15 familiar to those skilled in the art, such as laser ablation of a target material, solution synthesis or chemical vapor deposition.

While the particular technique used to produce nanostructures is not essential to the practice of the present invention, a brief description of the production of such nanostructures is given below for purposes of illustration.

20 Numerous nanostructure materials are contemplated by the present invention. For example, nanostructures formed from silicon (Si), germanium (Ge) and aluminum (Al), silicon oxide and germanium oxide are specifically contemplated.

According to typical laser ablation techniques, a target is placed within a chamber. Preferably, the target contains a suitable catalyst such as iron (Fe) or gold (Au). The 25 chamber is evacuated and then filled with inert gasses such as argon. The target is heated and then ablated with a suitable energy source such as a pulsed laser.

As the target is ablated, nanostructure-containing material is recovered from the vaporized target.

-5-

The nanostructure materials formed according to the technique described above are generally either cage-like spherical particles or rod/wire shaped objects having nanometer-scale dimensions.

For example, silicon nanostructures may comprise rod or wire-like shapes having a 5 diameter on the order of 1-50 nm and a length on the order of 0.5-10 μm . Figure 1 is a TEM micrograph of silicon nanostructures formed by a laser ablation technique. Figure 2 is an x-ray diffraction pattern of these silicon nanostructures. The FeSi₂ peaks are caused by the Fe catalysts present in the Si target. Moreover, the outer surfaces of the nanostructure objects are typically covered by thin layers of silicon oxides.

10 Nanostructures apparently have higher surface to volume ratio than the bulk material from which they are derived or from other forms of the material such as whiskers (see, for example, R.S. Wagner and W.C. Ellis in *Appl. Phys. Lett.*, Vol. 4, page 89, 1964 for the synthesis of Si whiskers).

15 The nanostructures are more reactive and may also have a lower melting temperature than the bulk materials. Therefore nanostructures formed of various materials such as Si, Ge, and Al exhibit increased reactivity and increased ability to reversibly react with alkali metals such as lithium.

20 For instance, Figure 3 illustrates another difference between bulk materials and nanostructures formed therefrom. As shown in Figure 3, the spectrum from bulk crystalline Si is compared with that of nanostructured Si. The characteristic Si sp³ stretching mode for nanostructured Si is slightly down-shifted from that of bulk crystalline Si.

One suitable technique for producing silicon nanostructures is described in A.M. Morales and C.M. Lieber, A Laser Ablation Method for the Synthesis of Crystalline Semiconductor Nanowires, *Science*, 279, 208-211, 1998; and Y.F. Zhang and et al., Silicon nanowires prepared by laser ablation at high temperature, *Appl. Phys. Lett.*, 72, 15, 1835-25 1837, 1998.

Similarly, Figure 4 illustrates the characteristic Ge sp³ stretching mode of nanostructured Ge as being slightly down-shifted from that of the bulk crystalline Si.

30 Nanostructured Ge was synthesized using the laser ablation method (e.g.- Morales and Lieber, *Science* vol. 279, 208-211, 1998). Target composed of Ge and Fe (10atm.%)

-6-

was ablated by a pulsed Nd:YAG laser at 900C under a constant flow of argon. Electron microscopy measurements show that thus synthesized materials comprise both Ge nanowires with an average diameter of 5-30nm and micron in length, and nanoparticles with the average diameter of 1-50nm.

5 Another advantage of the nanostructure materials of the present invention is that they can be rather easily deposited as a film onto a substrate material. For example, as illustrated in Figure 5, a sample of purified nanostructure material can be solution-deposited to form a coating 12 on an appropriate substrate.

10 Nanostructure-based materials of the present invention unexpectedly possess specific lithium storage capacities that exceed those possessed by conventional carbon-based materials.

15 As described in the Background, in a testing electrochemical cell, the lithium ions travel from the lithium electrode to the nanostructure material electrode during discharge. The lithium ions are readily accepted into the large surface area of the nanostructure material. When a lithium ion is accepted into the nanostructure material according to the present invention a chemical reaction takes place, even at temperatures on the order of 300°K and a distinct lithium-nanostructure material phase is formed, thus forming an "alloy" therewith. This reaction acts as a storage mechanism that enables the material to hold a charge (i.e.-in the form of lithium ions). As noted above, nanostructure materials exhibit 20 increased reactivity. For example, while conventional macroscopic silicon must be heated to a temperature on the order of 400°C to react with lithium (see, for example, R.N. Seefurth and R.A. Sharma, Investigation of lithium utilization from a lithium-silicon electrode, *J. Electrochem. Soc.*, Vol. 124, No. 8, 1207-1214, 1977; C.J. Wen and R.A. Huggins, Chemical diffusion in intermediate phase in the lithium-silicon system, *J. of Solid State. Chem.*, 37, 271-278 (1981).), the silicon nanostructure material of the present invention 25 electrochemically reacts with lithium at room temperature or even lower.

The energy density, or ability of the silicon nanostructure material of the present invention to accept foreign species, such as alkali metals, and more specifically lithium, was measured by constructing a electrochemical cell, similar to that described in the Background

section above. An electrochemical cell incorporating the silicon nanostructure-based material of the present invention is schematically illustrated in Figure 6.

A cell was constructed with a lithium foil electrode 20 and a stainless steel substrate plate 10 having a nanostructure film 12 deposited thereon, as the second electrode. A 5 polypropylene filter soaked with an electrolyte 22 was placed between the two electrodes. Electrical contacts were made by two stainless steel plungers 24, 26 pressed against the electrodes. A current source 28 is connected to the plungers. The cell was then discharged and charged.

The nanostructure-lithium materials of the present invention have significantly 10 higher capacities than conventional materials. For example, the silicon nanostructure-lithium materials of the present invention have exhibited capacities of 1500mAh/g in the first discharge cycle, reversible capacities on the order of at least 900mAh/g to at least approximately 1,000mAh/g and an irreversible capacity of less than 500mAh/g. Lithium discharge occurs at essentially a constant voltage below 0.1V. Most of the lithium can be 15 removed from the nanostructured silicon electrode at below 0.5V.

Figure 7 is a voltage-capacity plot for a fully lithiated silicon nanostructure sample that showed a total capacity of approximately 1300mAh/g. The reversible part, defined as the capacity displayed after the second discharge, is approximately 800mAh/g. The inset of Figure 7 illustrates the capacity of the material versus the number of charge-discharge

20 cycles. Figure 8 illustrates x-ray diffraction and Raman spectrum data collected from a Si nanostructure electrode at different stages of the first discharge cycle.

The x-ray and Raman intensities from the nanostructured Si decreases with increasing Li concentration and vanished in the fully lithiated state(spectra a, b and c). The characteristic Si sp³ stretching mode re-appeared in the Raman spectrum in the electrode at 25 the end of the first charge (spectrum d), indicating recovery of sp³ Si after extraction of Li. Inset shows the voltage versus capacity data from the same cell and the integrated x-ray intensity ratio of the Si (111) and FeSi2 peaks (FeSi2 is inert to Li and is used as the internal reference).

Figure 9 illustrates the second-cycle charge-discharge data from a sample containing 30 nanostructured Ge and Ge oxide, after vacuum annealing at 150°C. The data were collected

-8-

under galvanostatic mode using 50mA/g rate at 300K. The reversible Li capacity is 1500mAh/g (normalized with the total sample weight, the value will be higher than the total capacity is normalized with weight of nanostructured Ge, excluding the Fe catalysts). A distinct voltage step is present during both Li insertion and extraction.

5 Another important performance parameter is how the rate of charging and discharging affects the capacity of the material. Some applications, such as electrical vehicles, require the electrode material to operate under high rate charging and discharging conditions. Generally, the capacity of the material decreases with an increased rate. The nanostructure-lithium material of the present invention exhibits high capacities, even when charged/discharged at high rates.

10 Yet another important performance parameter is the electrochemical potential with respect to Li. For example, lithium insertion into the current Si nanostructure based material occurs below 0.1V and lithium extraction takes place mostly below 0.5V. This means that the nanostructured silicon based materials can replace the current carbon based negative electrodes in the Li-Ion batteries without reduction in the cell voltage.

15 According to the present invention, it is also possible to further increase the Li storage capabilities of the nanostructure materials through addition processing of the material. For example, nanostructured Si samples from the same batch were annealed at different temperatures (200-900C) under 5×10^{-6} torr vacuum. Their charge/discharge characteristics were measured under the same conditions as described above. The total discharge and reversible Li capacities were found to initially increase with the annealing temperature up to ~600C then decrease with further increase of the annealing temperature. Annealing is believed to remove chemical species on the surfaces of nanostructured Si. These chemical species and oxide coating can also be removed by other processes such as 20 hydrogen plasma.

25 The excellent capacity of the nanostructure-based materials of the present invention, combined with their superb mechanical and electrical properties, and the ease of forming films, make them attractive electrode materials for high energy density batteries (e.g.-high energy density Li-ion batteries), batteries for high current rate applications, and thin-film 30 batteries.

-9-

Although the present invention has been described by reference to particular embodiments, it is in no way limited thereby. To the contrary, modifications and variants will be apparent to those skilled in the art in the context of the following claims.

-10-

WHAT IS CLAIMED IS:

1. A material comprising a nanostructure and a foreign species, said material having a reversible capacity of at least 900 mAh/g.

5

2. The material of claim 1, wherein the material is silicon-based and comprises silicon nanostructures.

10 3. The material of claim 1, wherein said nanostructure comprises at least one of a rod, wire-like shape, or spherical particles.

4. The material of claim 3, wherein the rod or wire-like shape has a diameter of about 1-50nm and a length of about 0.5-10 μ m.

15 5. The material of claim 1, wherein the foreign species comprises alkali metal.

6. The material of claim 5, wherein the alkali metal comprises lithium.

20 7. The material of claim 1, wherein the reversible capacity is at least 1,000mAh/g.

8. The material of claim 7, wherein the material is germanium-based and comprises germanium nanostructures.

25 9. The material of claim 1, further comprising an irreversible capacity of less than approximately 500mAh/g.

10. A material comprising at least one of germanium and silicon nanostructures, said material having a reversible capacity of at least 900mAh/g.

30

-11-

11. The material of claim 10, wherein the material has a reversible capacity of at least 1,000mAh/g.

12. The material of claim 10, wherein the material has an irreversible capacity of
5 less than 200mAh/g.

13. An article of manufacture comprising:
an electrically conductive substrate; and
a film disposed on said substrate, said film comprising the material of claim
10 10.

14. The article of claim 13, wherein said substrate comprises an electrically conductive metal.

15. The article of claim 13, wherein said article comprises an electrode.

16. A germanium-based material and a foreign species comprising a germanium and germanium oxide nanostructure and a foreign species, said material having a reversible capacity of at least 1,000 mAh/g.

20

1/7

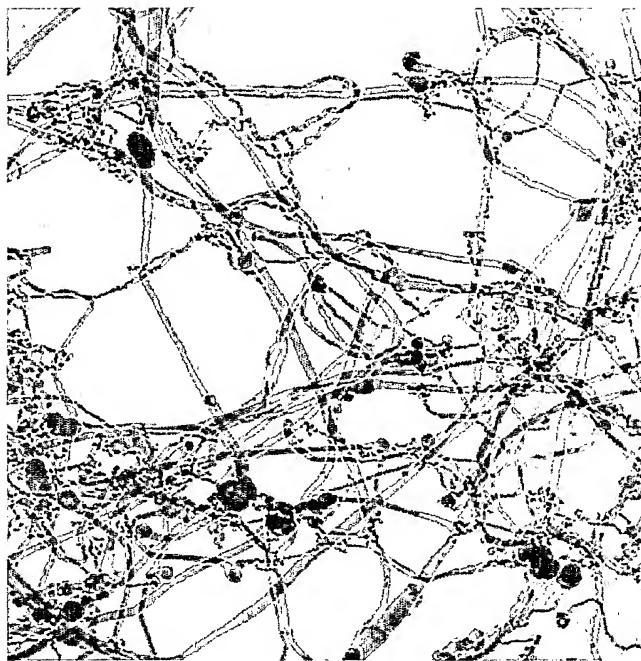
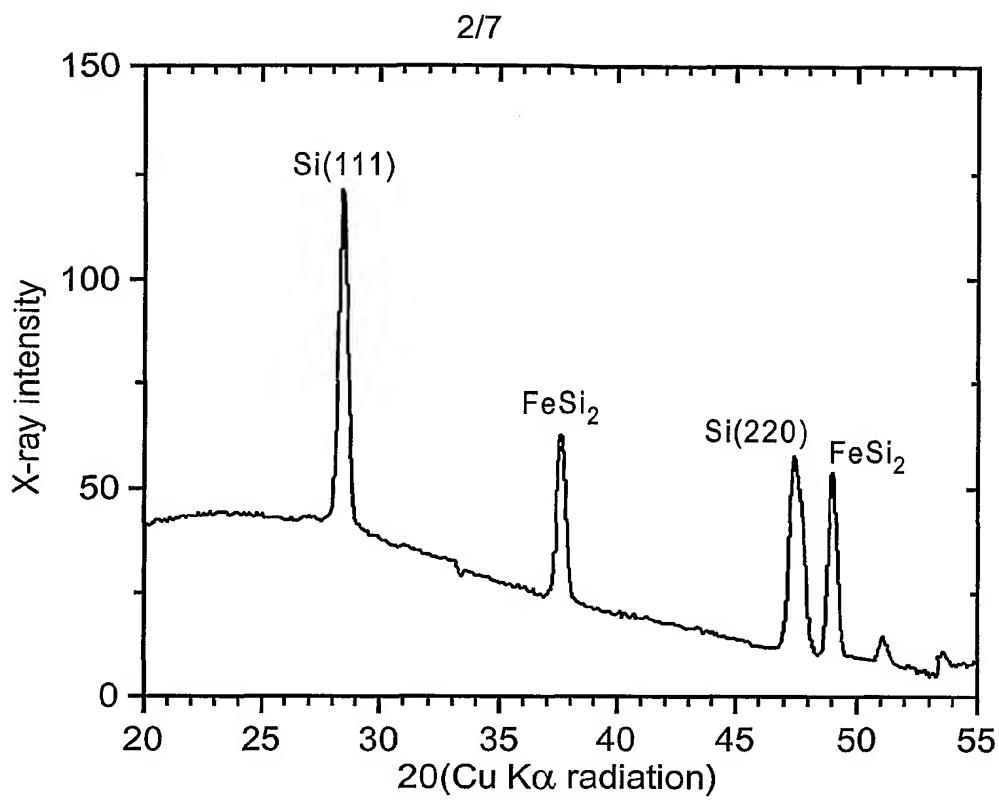
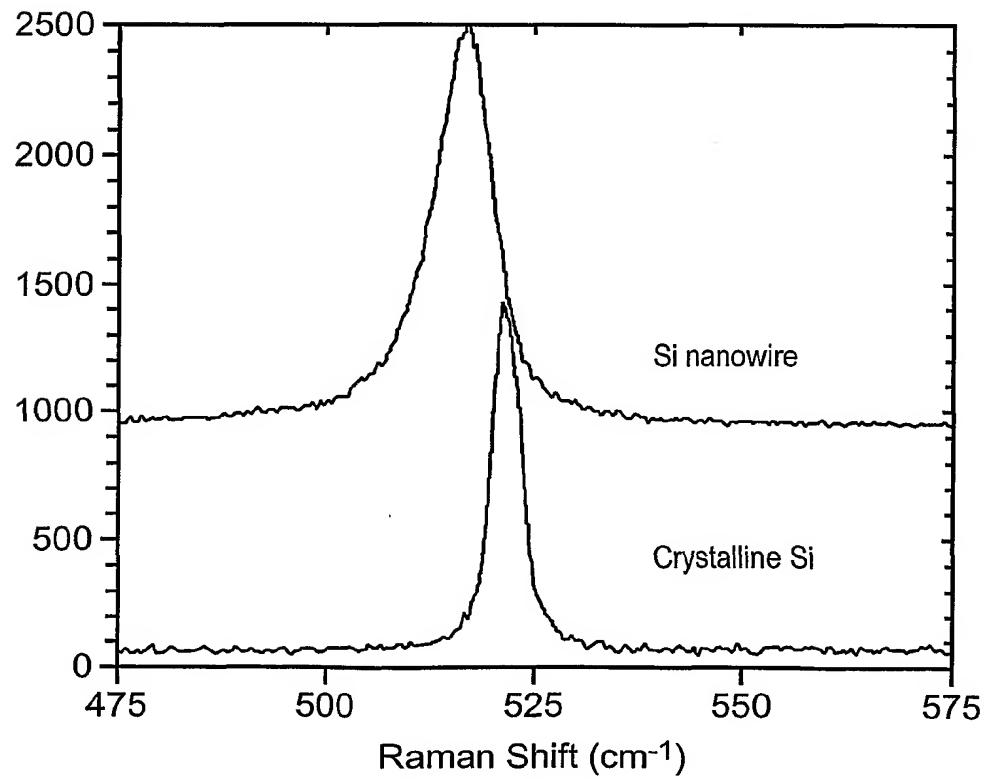


FIG. 1

**FIG. 2****FIG. 3**

3/7

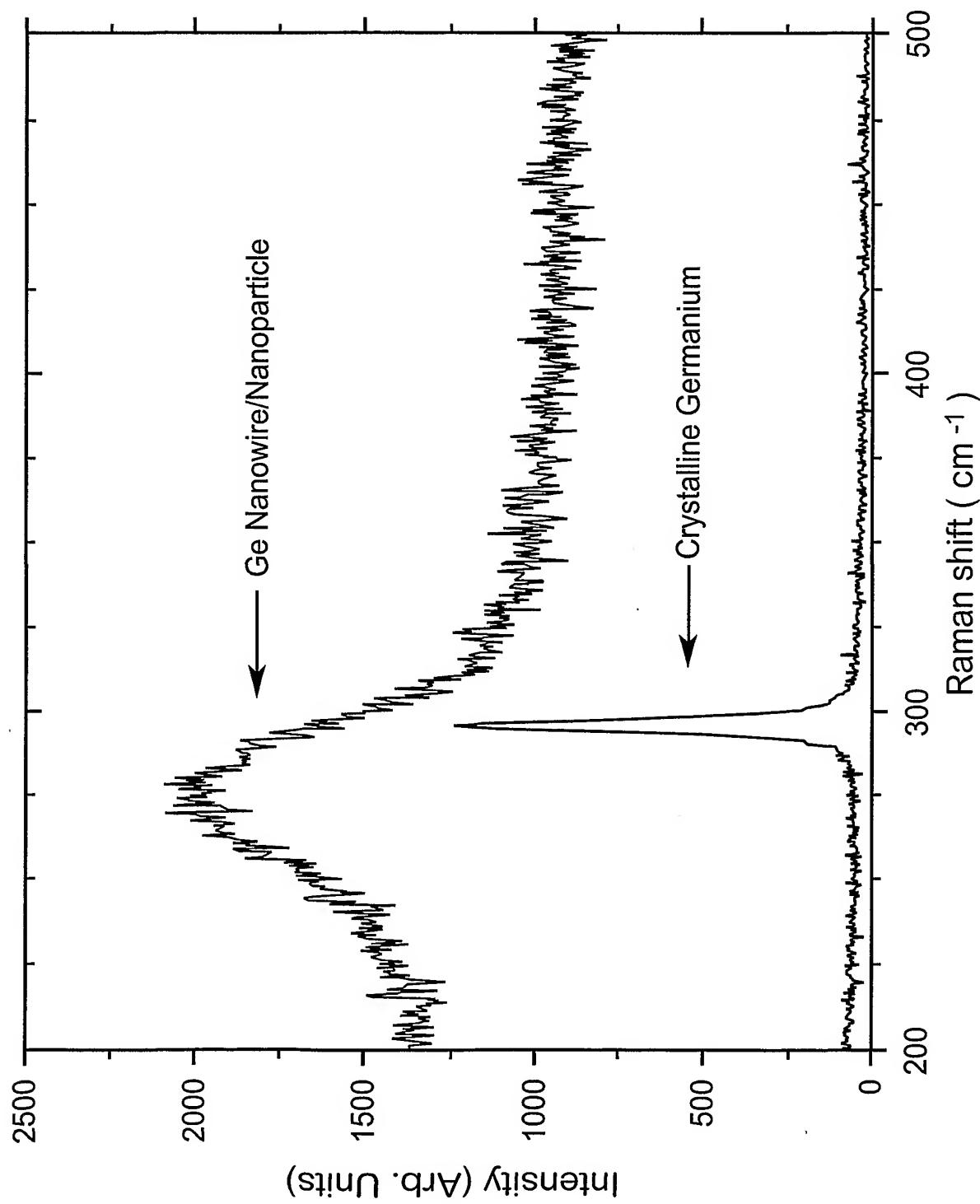


FIG. 4

4/7

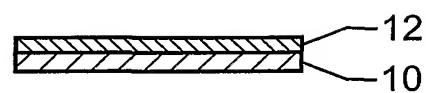


FIG. 5

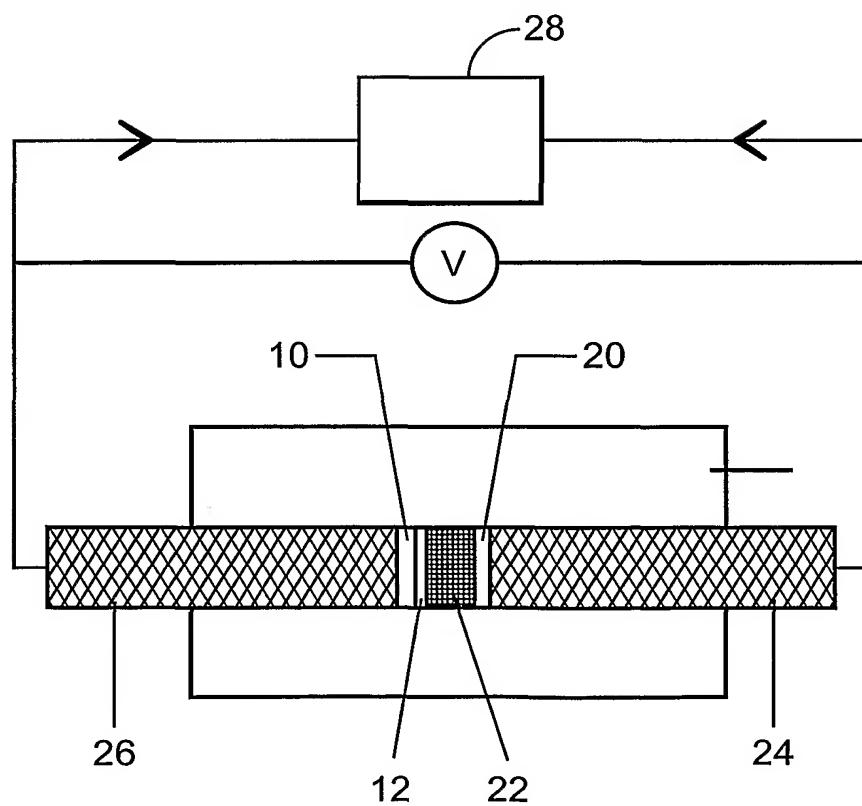


FIG. 6

5/7

FIG. 7

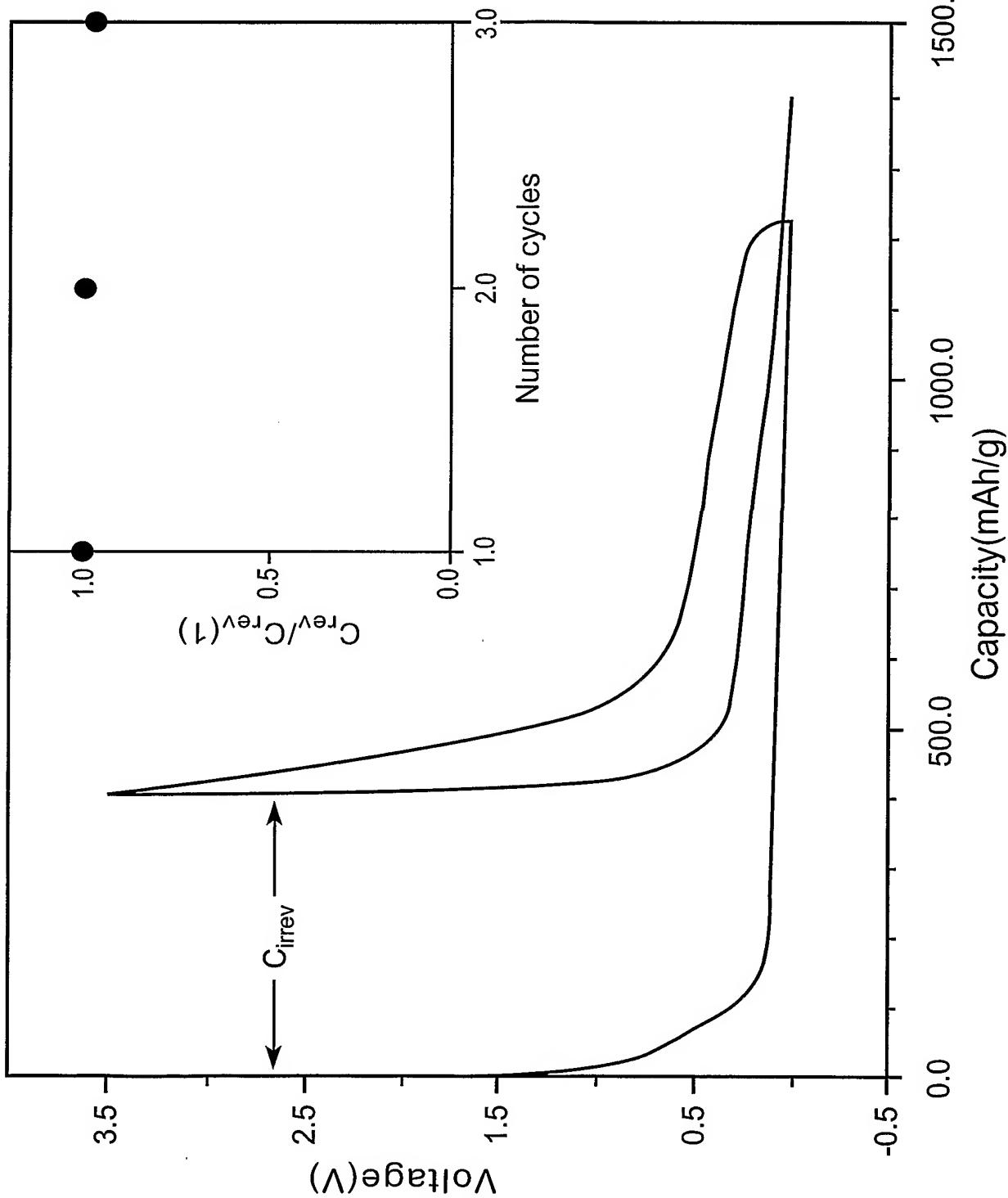
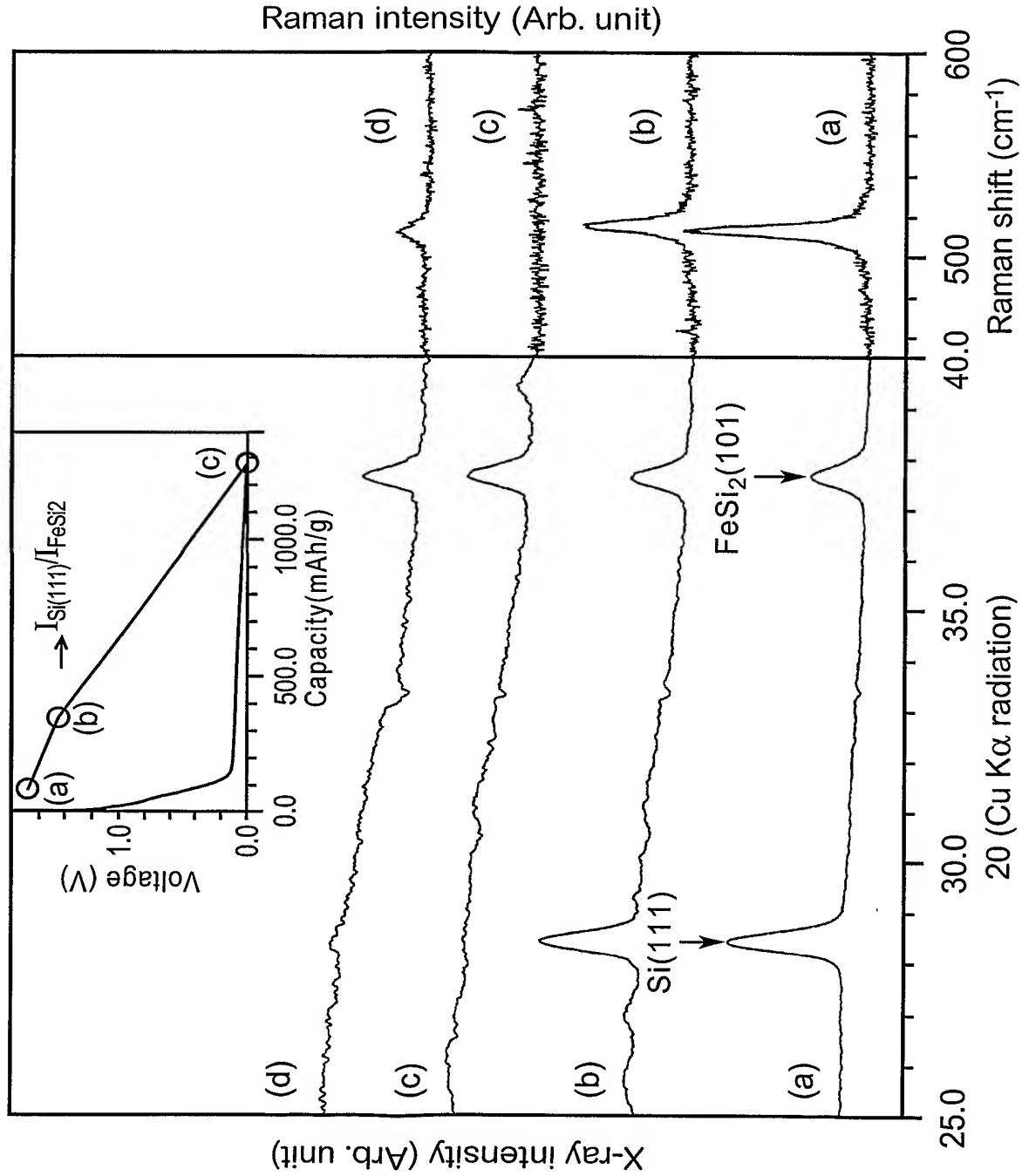


FIG. 8



7/7

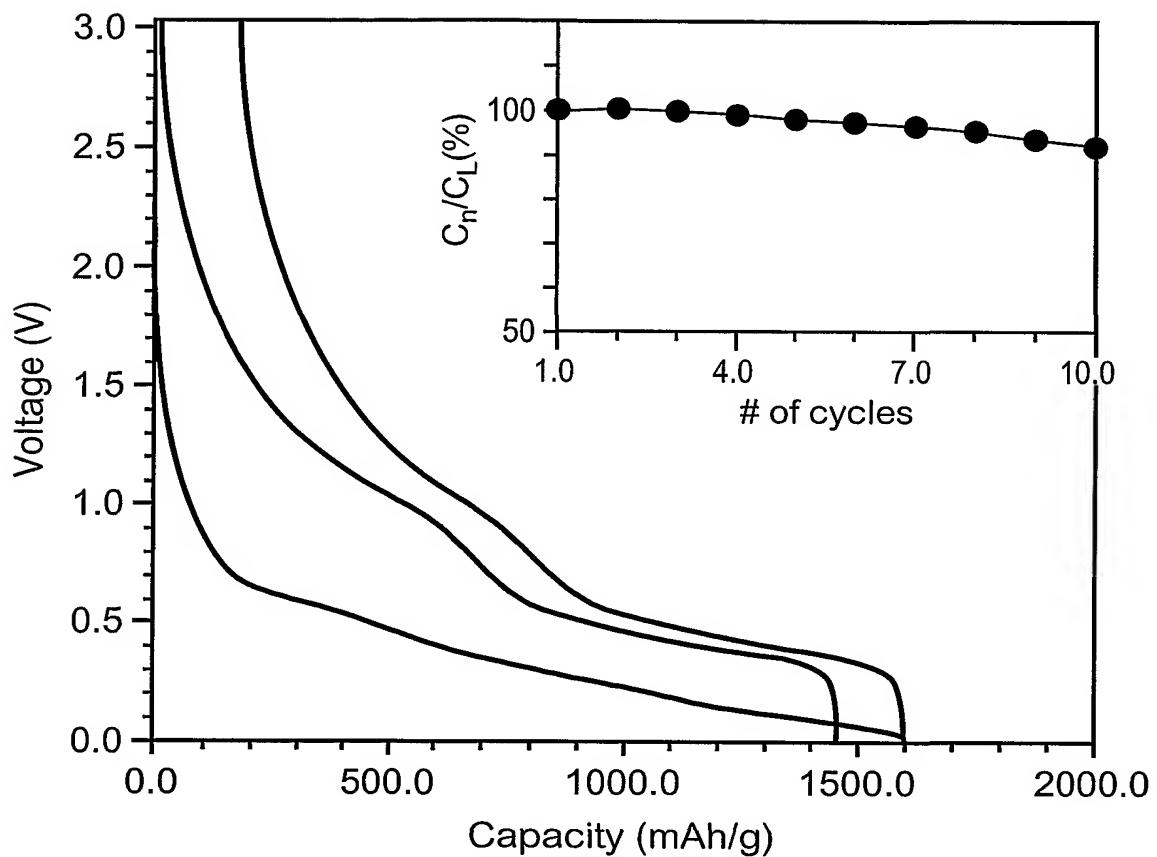


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/18846

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : G01N 27/26; HO1L 29/41, 29/48; D01F 9/12; C01B 31/80
US CL : 204/409, 410, 421; 423/345, 346; 257/741, 742

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/409, 410, 421; 423/345, 346; 257/741, 742

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,997,832 A (LIEBER et al) 7 December 1999, col. 4, lines 34-36 , lines 50-54, col. 3 lines 24-30, lines 50-58, col. 5 line 19.	1-9, 10-12
Y	US 5,457,343 A (AJAYAN et al) 10 October 1995, col. 3, lines 22-26 & 34, col. 6 line 12.	1-16
A	US 5,338,430 A (PARSONAGE et al) 16 August 1994, Abstract	
A	US 5,587,256A (WILSON et al) December 1996.	
X	G. W. ZHOU et al, "Controlled Li doping of Si nanowires by electrochemical insertion method", Applied Physics Letters, Vol 75, No. 16, October 18, 1999, page 2447-2449.	1-3, 5-7, 10-11, 17

Further documents are listed in the continuation of Box C. See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

06 SEPTEMBER 2001

Date of mailing of the international search report

15 NOV 2001

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305 0200

Authorized officer

CATHY LAM

Telephone No. (703) 305 0200

INTERNATIONAL SEARCH REPORT

International application No. PCT/US01/18846

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	J. R. Dahn, "Mechanisms for Lithium Insertion in Carbonaceous Materials", Science, Vol. 270, October 27, 1995, page 590-593.	
A	R. N. Seefurth et al., "Investigation of Lithium Utilization from A Lithium-Silicon Electrode", J. Electrochem Soc., Vol. 124, No. 8, August 1977, page 1207-1214.	
A	A. M. Morales et al., "A Laser Ablation Method for the Synthesis of Crystalline Semiconductor Nanowires", Science, Vol. 279, January 9, 1998, page 208-211.	
A	Y. F. Zhang et al., "Silicon nanowires prepared by laser ablation at high temperature", Applied Physics Letters, Vol. 72, No. 15, April 13th, 1998, page 1835-1837.	
A	C. John Wen et al., "Chemical diffusion in Intermediate phases in the Lithium-Silicon System", Journal of Solid State Chemistry, Vol. 37, 1981, page 271-278.	
A	M. Winter et al., "Insertion Electrode Materials for Rechargeable Lithium Batteries" Advanced Materials, Vol. 10, 1998, page 725-262.	
A	M. S. Whittingham (Editor), "Recent Advances in Rechargeable Li Batteries" Solid state Ionics, Vol. 69, No. 3, 4, 1994.	
A	G. Pistoia (Editor), "Lithium Batteries: New Materials, Developments and Perspectives", Industrial Chemistry Library, Vol. 5, Elsevier, 1994.	
A	A. M. Wilson et al, "Carbonaceous Materials Containing Silicon as Anodes for Lithium-ion Cells" Mat. res. Soc. proc., Vol. 393, 1995, page 305-313.	